Preparation, Characterization, and Chromium(II) Reduction of the Linkage Isomers of Formamidopentaamminecobalt(III)

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Abstract: The linkage isomers of formamide with oxygen and nitrogen bonded to pentaamminecobalt(III) have been prepared. Visible, ir, and nmr spectroscopy have been used to assign the isomers. The nitrogen-bonded isomer is a moderately strong acid, due to the equilibrium $(NH_3)_5CoNH_2CHO^{3+} \rightleftarrows (NH_3)_5CoNHCHO^{2+} + H^+$ which has a K_a of 6.92×10^{-3} *M* (25.5°; μ, 0.92 *M*) with $\Delta H = -4.8$ kcal mol^{-1} and $\Delta S = -25$ eu The nmr spectrum of the conjugate base of the N-bonded isomer provides evidence for restricted rotation about the C–N bond. The chromium(II) reduction of the N-bonded formamide complex has the rate law $-d \ln [(NH_3)_5CoNH_2CHO]/dt = k'[Cr^{2+}]/[H^+]$. If reduction proceeds through the conjugate base of the N-bonded isomer then $k' = k_{NH}K_a$. The known values of K_a and k' were used to calculate a value of 1.74 M^{-1} sec^{-1} for k_{NH} at 25.5°, with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 12.0 kcal mol^{-1} and −17 eu, respectively. The reduction was found to proceed with ligand transfer to give O-bonded formamidopentaaquochromium(III). The chromium(II) reduction of the O-bonded isomer proceeds without ligand transfer to chromium. The rate is first order in cobalt complex, first order in chromium(II), and independent of $[H^+]$, with $k = 8.5 \times 10^{-3}$ M^{-1} sec^{-1} (26.0°; μ, 1.0), $\Delta H^{\ddagger} = 10.7$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -32$ eu. Almost identical results have been found for the O-bonded N,N-dimethylformamide for which $k = 6.7 \times 10^{-3}$ M^{-1} sec^{-1} (25.0°, μ, 1.0, by extrapolation), $\Delta H^{\ddagger} = 10.6$ kcal mole^{-1}, and $\Delta S^{\ddagger} = -33$ eu.

Several recent studies[1] have made use of the phenomenon of linkage isomerism to help elucidate the mechanism of electron transfer reactions. In connection with the studies of Taube and coworkers[2] on the reductions of carboxylatopentaamminecobalt(III) complexes, it is often found that the reaction proceeds by a carboxylato bridge. That is, the reducing agent is apparently partially bonded in the transition state to the carboxyl group which is bonded to the cobalt(III). It has never been possible, however, to decide whether the reducing agent is bonding to the carbonyl (C=O) oxygen or to the oxygen which is bonded directly to cobalt(III).

In an attempt to answer this question the authors have prepared the nitrogen- and oxygen-bonded linkage isomers of formamidopentaamminecobalt(III), $[(NH_3)_5CoNH_2CHO]^{3+}$ (N isomer), and $[(NH_3)_5CoOCHNH_2]^{3+}$ (O isomer), as well as the conjugate base of the N isomer $[(NH_3)_5CoNHCHO]^{2+}$. It was expected that when these complex ions were reduced by chromium(II), if the reducing agent attacks at the ligand atom bonded to cobalt(III), then the O isomer should give an oxygen-bonded chromium(III) isomer, and the N isomer should give a nitrogen-bonded chromium(III) product. The opposite chromium(III) products would be expected if the chromium(II) attacks at the remote ligand atom. Unfortunately these ideal expectations have not been achieved and the N-bonded chromium(III) product has not been observed. The differences in reactions of the linkage isomers do indicate, however, some of the factors which are important in bridged electron transfer reactions.

Fraser[3] has reported previously a rate of reduction for formamidopentaamminecobalt(III) by chromium(II), but his results do not agree even qualitatively with those reported here. It would seem that Fraser was working with a mixture of isomers, but this does not entirely explain the discrepancy.

For purposes of comparison the temperature dependence of the chromium(II) reduction of N,N-dimethylformamidopentaamminecobalt(III) has been studied. The rate at 25° agrees well with that given by Gould.[4]

Experimental Section

Reagents. All solutions were prepared with water redistilled from alkaline permanganate in an all-glass apparatus. Standard solutions of lithium perchlorate were prepared by treating weighed samples of lithium carbonate with a slight excess of 70% $HClO_4$. After effervescence had ceased the solutions were heated to remove CO_2 and diluted with distilled water. Excess acid was determined by titration with standard NaOH.

Chromous perchlorate solutions were prepared by dissolving electrolytic chromium (99.999% purity, United Mineral and Chemical Corp.) in dilute perchloric acid. These solutions were analyzed for chromium(II) periodically by reacting an aliquot of the chromous solution with an excess of standard ferric ammonium sulfate solution, and the excess ferric ion was determined by addition of potassium iodide and titration of the iodine liberated with standard thiosulfate.

Oxygen was removed from all solutions by purging with nitrogen purified by passing through three scrubber solutions of chromous perchlorate over zinc amalgam. The solutions were handled using standard syringe techniques.

Preparation of Complexes. The conjugate base of the N isomer of formamidopentaamminecobalt(III) perchlorate was prepared by dissolving aquopentaamminecobalt(III) perchlorate in reagent grade formamide (20 g of aquopentaamminecobalt(III) perchlorate in 100 ml of formamide) and heating the solution on a steam bath for 4 hr. The resulting solution was mixed with a twofold excess of *sec*-butyl alcohol and the resulting precipitate of $[(NH_3)_5CoNHCHO](ClO_4)_2$ was collected by filtration, washed with ethanol and ether, and air-dried. Addition of more *sec*-butyl alcohol to the filtrate from above precipitates a pink crystalline material which has not been fully characterized as yet. The conjugate base was

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[1] (a) J. P. Birk and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 1153 (1968); (b) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

[2] H. Taube, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 107.

[3] R. T. M. Fraser, D. E. Peters, and G. T. Takaki, "Proceedings of the 8th Conference on Coordination Chemistry, Vienna," Springer-Verlag, Berlin, 1964, p 268.

[4] E. S. Gould, *J. Amer. Chem. Soc.*, **89**, 5792 (1967).

recrystallized three times from water. The absorption spectrum shows maxima at 250 mμ (ϵ 25,200), 348 (81.3), and 484 (68.4). In 1.0 M perchloric acid the protonated species $[(NH_3)_5CoNH_2CHO](ClO_4)_3$ predominates and shows absorption maxima at 340 mμ (ϵ 63.8) and 478 (62.2).

The $[(NH_3)_5CoNH_2CHO](ClO_4)_3$ species is easily precipitated from water with perchloric acid but is not readily obtained in pure solid form. It was found that washing the solid with 98% ethanol caused removal of a proton and yielded a mixture of the N-bound forms. Preliminary studies also indicate that the acid form of the N isomer isomerizes to the O isomer in the solid state.

Titration of a carefully prepared sample of $[(NH_3)_5CoNH_2CHO](ClO_4)_3$ with standard sodium hydroxide gave an equivalent weight of 493, compared to the calculated value of 487.5.

Anal. Calcd for $[(NH_3)_5CoNHCHO](ClO_4)_2$: C, 3.10; H, 4.43; N, 21.7. Found: C, 3.25; H, 4.43; N, 21.3.

Oxygen Isomer. This isomer was prepared through the intermediate trimethylphosphatopentaamminecobalt(III) complex.[5] Aquopentaamminecobalt(III) perchlorate (20 g) was dissolved in trimethyl phosphate (200 ml) with molecular sieve and the solution heated for 2 hr on a steam bath. Then the excess trimethyl phosphate was extracted with *t*-butyl alcohol leaving an oil of the trimethylphosphatopentaamminecobalt(III) perchlorate. This oil was dissolved in formamide (125 ml) and the solution was allowed to stand at ambient temperature for 2 hr. Addition of *sec*-butyl alcohol to this solution gave a precipitate which contained a mixture of products. This mixture was separated by cation exchange chromatography on Rexyn 102(H) (Fisher Scientific Co.) in sodium ion form, eluting with solutions of $NaHCO_3$, adjusted to pH 7.2, in increasing concentrations up to 1.0 M. This procedure gave a separation into three bands, the most strongly held being the O isomer of formamidopentaamminecobalt(III). Rather than eluting the complex from the column, it was found to be more efficient to separate the bands on the ion exchange resin physically. The resin was washed with water and then treated in a batch with enough concentrated perchloric acid to remove the complex. This process also released a considerable amount of water from the resin. The resin was removed from the solution containing the complex by filtration, and the complex precipitated by adding sodium perchlorate to the filtrate.

The visible absorption spectrum showed maxima at 346 mμ (ϵ 57.5) and 502 (68.8) in water and 1.0 M perchloric acid.

Anal. Calcd for $[(NH_3)_5CoOCHNH_2](ClO_4)_3$; C, 2.47; H, 3.73; N, 17.3. Found: C, 2.52; H, 4.10; N, 16.9.

N,N-Dimethylformamide Complex. The complex was prepared by heating aquopentaamminecobalt(III) perchlorate (20 g) in N,N-dimethylformamide (200 ml) for 3 hr on a steam bath. The product was precipitated from the reaction solution by adding *sec*-butyl alcohol. The complex was recrystallized five times by dissolving it in the minimum amount of water at ~50°, filtering the solution, and then cooling to ~5°. The product was collected by filtration and washed in the usual way with 95% ethanol and ether. The visible absorption spectrum showed maxima at 347 mμ (ϵ 66.7) and 506 (77.3). Gould[6] has reported maxima at 347 mμ (ϵ 62.5) and 505 (76.0).

Anal. Calcd for $[(NH_3)_5CoOCHN(CH_3)_2](ClO_4)_3$: C, 7.00; H, 4.32; N, 16.3. Found: C, 7.56; H, 4.37; N, 16.2.

Determination of Ionization Constant of Nitrogen Isomer. The equilibrium constant for the proton dissociation from $[(NH_3)_5CoNH_2CHO]^{3+}$ to give $[(NH_3)_5CoNHCHO]^{2+}$ was determined spectrophotometrically at 25.5°, 34.6°, and 44.4° at a wavelength of 318 mμ. Varying amounts of standardized perchloric acid solution were added to solutions of $[(NH_3)_5CoNHCHO](ClO_4)_2$ and lithium perchlorate (to adjust the ionic strength to 0.92 M). The spectra were determined using a Bausch and Lomb 505 spectrophotometer using a standard thermostated cell compartment. The method and treatment of data followed that outlined by Albert and Sergeant.[7]

Kinetic Measurements. The spectrophotometer cell and reagent solution containers were all sealed with rubber serum caps and flushed with deoxygenated nitrogen. Reagents were all handled and mixed using standard syringe techniques.

All reactions were run under pseudo-first-order conditions (reductant in a 15–20-fold excess over oxidant). The observed rate constant was determined from the slope of a plot of log $(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ are the absorbancies at time t and after the reaction is complete. Only those plots of the rate data which were linear to at least 90% of reaction were used.

The extent of reaction was determined from the decrease in absorbance with time at 478 mμ. The rates at 25.5° were measured using a Cary Model 14 spectrophotometer, and all others were determined using Bausch and Lomb 505 and Precision spectrophotometers.

The temperature of the reaction solution in the spectrophotometer cell was controlled by pumping water from a Colora constant temperature bath through a specially bored aluminum cell holder. The temperature of the bath was regulated by a Fisher Thermistemp controller, with the thermistor probe inserted in the cell holder next to the spectrophotometer cell.

Ion Exchange Separation of Reaction Mixtures. Reaction mixtures from several of the kinetic runs and from 20 to 30 reactions carried out at Cr(II):Co(III) ratios of approximately 1:1 were ion-exchanged at 5° using Dowex 50W-X12 cation exchange resin. The resin was pretreated with 30% $HClO_4$, distilled water, 50% acetone, ethanol, and distilled water in order to remove all traces of organic material. Elution was carried out with perchloric acid, slowly increasing the concentration from 0.5 to 1.0 M to facilitate good separations. This was followed with a solution 0.5 M in $NaClO_4$ and 0.2 M in $HClO_4$, which gave rapid elution of the products from the ion exchange column. All products were characterized spectrophotometrically on a Cary Model 14 spectrophotometer. The extinction coefficients were calculated on the basis of the chromium concentration which was determined spectrophotometrically as chromate. Under optimum conditions the total time spent on the ion exchange column was about 90 min.

Nmr Measurements. The proton magnetic resonance spectra were obtained using a Varian A56/60 spectrometer and a Varian HA100 spectrometer. Spectra were recorded in deuterated dimethyl sulfoxide (DMSO), D_2O, and trifluoroacetic acid, with external TMS as the reference. All complexes in DMSO were the perchlorate salts, whereas chloride salts were used in D_2O, and chloride and trifluoroacetate salts in trifluoroacetic acid.

Infrared Measurements. All measurements were made using a Perkin-Elmer 421 grating spectrophotometer, using potassium bromide disks and Nujol mulls.

Results

Before considering the results in detail it seems appropriate to discuss the evidence which shows that the compounds being studied are linkage isomers. The analytical data show the expected ratio of C:H:N and serve to distinguish the formamide complexes from $Co(NH_3)_6(ClO_4)_3$ and $[Co(NH_3)_5O_2CH](ClO_4)_2$. The latter complexes might be formed from likely impurities in the formamide. The infrared and nmr spectra of the compounds show all the features expected and further establish that one is dealing with two formamide complexes.

The decision as to which is the O- and which is the N-bonded isomer is somewhat more difficult. The color and visible spectrum of the O isomer are consistent with that of other O-bonded pentaamminecobalt(III) complexes. Similarly the N-bonded isomer has the expected color and spectrum. This qualitative distinction also applies to the well-known nitro–nitritopentaamminecobalt(III) complexes. The nmr spectra are not particularly useful for this purpose, but the positions of the four *cis* and one *trans* NH_3 proton resonances are consistent with the isomer assignment given. This is based on comparison to the nmr spectra of known N- and O-bonded pentaamminecobalt(III) complexes. For the O-bonded complexes the resonance of the *trans*-NH_3 occurs at τ 7.2–7.3, while for the N-bonded complexes it occurs at τ ~6.8. For example, the *trans*-NH_3 resonance in formatopenta-

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[5] The method used in this preparation is based on the assumption that the O isomer forms first in formamide and then isomerizes with release of a proton to $(NH_3)_5CoNHCHO^{2+}$. Thus mild conditions would be necessary to prepare the O isomer.

[6] E. S. Gould, *J. Amer. Chem. Soc.*, **90**, 1740 (1968).

[7] A. Albert and E. P. Sergeant, "Ionization Constants of Acids and Bases," John Wiley & Sons, Inc., New York, N. Y., 1962.

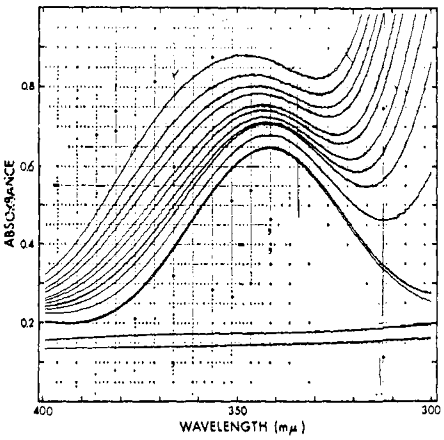

Figure 1. Absorption spectrum of $(NH_3)_5CoNH_2CHO^{2+}$ at 25.5°, μ = 0.92 M ($LiClO_4$) and varying $HClO_4$. The absorbance decreases as $[H^+]$ increases. Curves shown cover the range from 0.0015 to 0.923 M $HClO_4$.

amminecobalt(III) is at τ 7.28, whereas in the N-bonded sulfamatopentaamminecobalt(III) complex the peak occurs at τ 6.79. The parent hexaamminecobalt(III) has a resonance at τ 6.75 due to the six equivalent NH_3 groups.

The infrared spectra of the isomers are also consistent with, but do not definitively establish, the isomer assignment which has been given.

The strongly acidic character of one of the formamide isomers provides perhaps the best evidence for deciding which is the O- and which the N-bonded isomer. Only the N-bonded isomer would be expected to be acidic because of the proximity of $(NH_3)_5Co^{3+}$. The effect is analogous to that observed for the sulfamate[8] complex. The large difference in the visible spectra of the acid and base forms of this isomer shows that the proton is being removed from the atom adjacent to the cobalt(III).

Acid Dissociation Constant of N Isomer. The effect of changing hydrogen ion concentration on the spectrum of the N isomer is shown in Figure 1. This change is interpreted in terms of the equilibrium

$$(NH_3)_5CoNH_2CHO^{3+} \overset{K_a}{\rightleftarrows} (NH_3)_5CoNHCHO + H^+ \quad (1)$$

For a system such as this it is easily shown that a plot of $(\epsilon_{obsd} - \epsilon_2)[H^+]$ $vs.$ ϵ_{obsd} should be linear with slope $(-K_a)$ and intercept $(K_a\epsilon_1)$, where ϵ_1 and ϵ_2 are the molar extinction coefficients of the base and acid forms of the complex, and ϵ_{obsd} is obtained in the usual way from the observed absorbance and the total complex concentration. The appropriate plot of the data at 25.5° is shown in Figure 2. Somewhat different values of K_a were obtained from plots at other wavelengths; for example, data at 366.4 mμ gave a pK_a of 2.21 compared to 2.16 obtained at 318.4 mμ. The latter value is considered more reliable because there is a larger absorbance change at 318 mμ.

Potentiometric titration of the acid form of the N isomer with sodium hydroxide gave a pK_a of 2.4 at 25° and μ = 0.1. This value was determined from the pH at half-neutralization and is therefore not very reliable for such a strong acid, but does give qualitative confirmation of the spectrophotometric value.

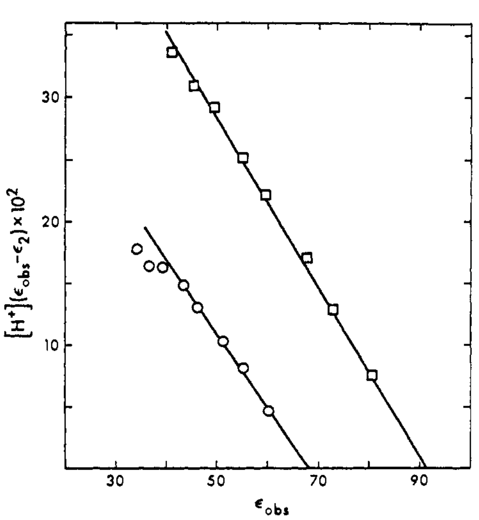

Figure 2. Determination of the acid dissociation constant (K_a) for $(NH_3)_5CoNH_2CHO^{3+}$ from the change in absorbance at 318.4 mμ (□) and 366.4 mμ (○) at 25.5°; μ, 0.92 M. ϵ_2 is the molar extinction coefficient of $(NH_3)_5CoNH_2CHO^{3+}$ and ϵ_{obsd} is the observed molar extinction coefficient.

The pK_a was also determined spectrophotometrically at 349 mμ and low ionic strength (0.06 M). An average value of 1.63 was obtained from two determinations at 25.5°.

Infrared Spectra. The infrared spectra of the O- and N-bonded isomers and the conjugate base of the N isomer were recorded in KBr disks and Nujol mulls. The chloride and perchlorate salts and the deuterated complexes were used. The spectra show the characteristic vibrations of coordinated NH_3 in the 1600, 1315, and 830 cm^{-1} regions.[9] Both of the N-bonded complexes show the characteristic aldehyde C–H bands at 2700 and 2780 cm^{-1}. The C–H stretch in the O-bonded isomer was less intense and broader and a definite assignment was not possible. In both isomers there are several bands in the 1300–1450 cm^{-1} region, which may be due to the amide N–H stretch, but it is not possible to make an unequivocable assignment of the vibration.

Deuteration of the isomers causes the broad ammonia absorption at 1600 cm^{-1} to shift to about 2400 cm^{-1}, permitting the carbonyl stretching frequency to be readily observed. Table I lists the carbonyl stretching frequencies for the bound and free formamide and for N,N-dimethylformamide.

Table I. Carbonyl Stretching Frequencies of Free and Complexed Ligand

Complex	C═O stretching frequency, cm^{-1} [a] Bound	Free
$(NH_3)_5CoNHCHO^{2+}$	1600	1716[b]
$(NH_3)_5CoNH_2CHO^{3+}$	1675	1716[b]
$(NH_3)_5CoOCHNH_2^{3+}$	1675	1716[b]
$(NH_3)_5CoOCHN(CH_3)_2^{3+}$	1655	1681[c]

[a] Spectra of the deuterated form of the complex in KBr disks and Nujol mulls show the same C═O frequency. [b] R. G. Puranik and K. Venkata Ramiah, *J. Mol. Spectrosc.*, **3**, 486 (1959). [c] J. Archambault and R. Rivest, *Can. J. Chem.*, **38**, 1331 (1960).

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(8) L. L. Po and R. B. Jordan, *Inorg. Chem.*, **7**, 526 (1968).

(9) (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963; (b) G. F. Siratos, D. M. Sweeny, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **79**, 3313 (1957).

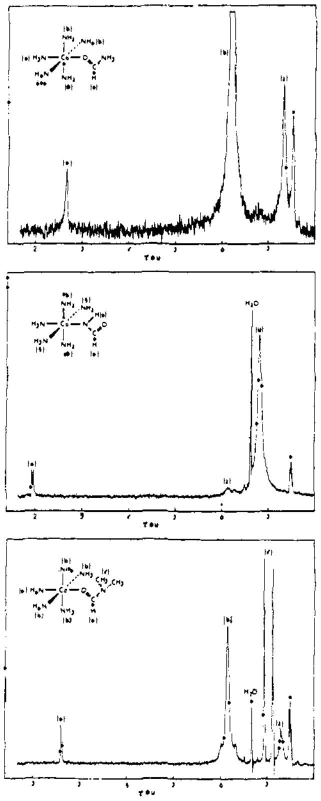

Figure 3. Pmr spectra in d_6-dimethyl sulfoxide. An asterisk denotes peak due to solvent. τ values are given in Table II.

The large differences in the carbonyl stretching frequencies of the acidic and basic forms of the N isomer may be rationalized in terms of the π bonding in the N–C–O system. Such conjugation is possible in the basic form of the N isomer and electron withdrawal from the N atom is at least partially compensated for by delocalization from the C=O bond, with a resulting decrease in the C=O stretching frequency. In the acidic form of the N isomer all orbitals on the nitrogen are used in σ bonding and the nitrogen is no longer in conjugation with the C=O system. Therefore the C=O stretch is much less affected by the $(NH_3)_5Co^{3+}$.

In the O isomer and the DMF complex, electron withdrawal from the C=O bond can be compensated for by electron donation from NH_2 and $N(CH_3)_2$ through the N–C π bond, with a resultant smaller decrease in the C=O stretching frequency.

Proton Magnetic Resonance Spectra. The observed chemical shifts for the formamide isomers and the DMF complex are given in Table II. The spectra in d_6-DMSO are shown in Figure 3.

In the case of the N isomer the specific assignments can be made reasonably unambiguously by comparison to formamide[10] and other pentaamminecobalt(III) complexes.[11]

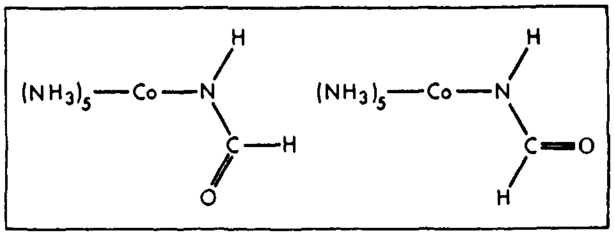

Figure 4. Rotational isomers of $(NH_3)_5CoNHCHO^{2+}$.

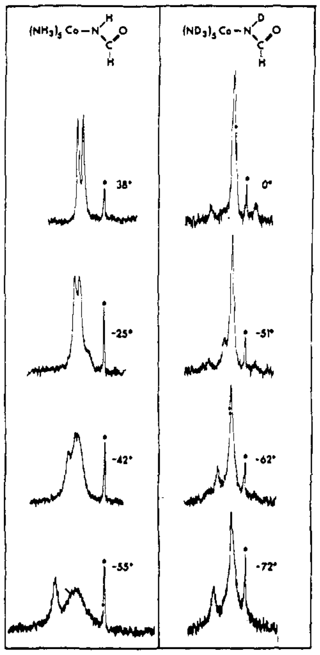

Figure 5. Temperature variation of the C–H pmr, in d_7-DMF, of $(NH_3)_5CoNHCHO^{2+}$ and $(NH_3)_5CoNDCHO^{2+}$. An asterisk denotes solvent peak due to formyl C–H in DMF.

The conjugate base of the N isomer may be expected to show two resonances for the C–H proton due to rotational isomerization about the M–C bond, as shown in Figure 4. A low temperature nmr study in d_7-DMF has confirmed the existence of these isomers. The spectra at several temperatures are shown in Figure 5, for the complex with a deuterium replacing the hydrogen atom on the nitrogen. The latter substitution simplifies the spectra by removing the proton–proton coupling in the C–H resonance. Qualitatively the changes in spectrum with temperature indicate that one rotational isomer predominates at high temperature, but the two are present in equilibrium at low temperature. As the temperature is lowered, a peak due to the second isomer begins to appear downfield from the other peak. The

Table II. Proton Chemical Shift Data

	Solvent	CH	NH_2	*cis*- NH_3	*trans*- NH_3
N Isomer	DMSO[e]	1.96[a]	6.14[b]	6.80	(6.80)[c]
basic	D_2O[f]	1.92		6.62	
N Isomer	DMSO[e]	2.66	6.18	6.68	(6.68)[c]
acidic	$F_3C_2O_2H$[f]	2.05	6.23	6.73	(6.68)[c]
O Isomer	DMSO[e]	2.62	(6.16)[c]	6.16	7.26
DMF[d]	DMSO[e]	2.60		6.14	7.28

[a] Doublet due to coupling with formamide NH proton, J = 3.8 Hz. [b] The N–H proton in the basic form of the N isomer. Assignment confirmed by spin decoupling of CH resonance. [c] Not observed, but assumed hidden under *cis*-NH_3 peak as indicated by integration. [d] CH_3 at τ 6.92 and 7.10. [e] Internal standard d_6-DMSO peak at τ 7.48. [f] External standard TMS.

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(10) B. Sunners, L. H. Piette, and W. G. Schneider, *Can. J. Chem.*, **38**, 681 (1960).

(11) R. Balahura, unpublished data.

relative intensity of the new peak increases, and its position shifts further downfield as the temperature decreases. A limiting spectrum cannot be obtained in DMF and therefore a quantitative analysis of the spectra in Figure 5 is not possible. Efforts are currently being made to find a solvent suitable for measurement of the limiting chemical shifts.

For the O-bonded complexes the nmr assignments can be made by comparison to other O-bonded complexes, in particular formatopentaamminecobalt(III). In the case of the O isomer of formamide no coupling between C-H and NH_2 was observed.

A temperature study was undertaken on the DMF complex to try to observe averaging of the two methyl resonances. In this case solvolysis to give the DMSO complex and free DMF occurred at about 55° and no merging of the CH_3 resonances was observed below this temperature.

Chromium(II) Reduction: Kinetics and Product Analysis. The stoichiometries of the chromium(II) reductions were determined by analyzing for the chromium(II) left after ten half-times for reaction solutions containing various initial chromium(II) to cobalt(III) ratios. The analysis was carried out by oxidation of chromium(II) with excess iron(III) and determining the excess iron(III) iodometrically. In all cases 1 mole of chromium(II) was consumed per mole of cobalt(III).

The reduction of the N isomer was found to follow the rate law

$$\frac{-\mathrm{d}\ln[(NH_3)_5CoNH_2CHO]}{\mathrm{d}t} = \frac{k'[Cr^{2+}]}{[H^+]} \qquad (2)$$

A summary of representative rate data is given in Table III. The plot of $k'/[H^+]$ *vs.* $[H^+]^{-1}$ (Figure 6) is linear as predicted by eq 2. This rate law is consistent with the mechanism

$$(NH_3)_5CoNH_2CHO \overset{K_a}{\rightleftharpoons} (NH_3)_5CoNHCHO + H^+$$

$$(NH_3)_5CoNHCHO + Cr^{2+} \xrightarrow{k_{NH}} \text{products}$$

Table III. Kinetic Data for the Reduction of $[(NH_3)_5CoNH_2CHO]^{3+}$ by Chromium(II)[a]

[Oxidant][b] × 10^2	[Reductant][b] × 10^2	$[H^+]$[b]	Temp, °C	$10^2 \times k_{obsd}$, M^{-1} sec^{-1}
0.21	3.32	0.760	25.5	1.12
0.19	3.70	0.750	25.5	1.27
1.05	16.78	0.500	25.5	2.02
1.05	16.78	0.405	25.5	3.10
0.86	16.78	0.280	25.5	4.00
0.86	15.10	0.250	25.5	4.60
0.99	16.55	0.197	25.5	5.70
1.06	16.55	0.190	25.5	6.14
1.08	23.02	0.170	25.5	7.00
0.21	3.70	0.750	34.4	2.20
0.22	3.70	0.475	34.4	3.86
0.21	3.70	0.270	34.4	6.14
0.22	3.70	0.198	34.4	8.00
0.25	3.79	0.188	34.4	8.80
0.21	3.70	0.750	44.6	3.80
0.21	3.39	0.475	44.6	5.89
0.25	3.79	0.465	44.6	6.36
0.21	3.39	0.270	44.6	10.20
0.21	3.39	0.198	44.6	14.00

[a] For all runs μ = 0.92 *M* ($LiClO_4$). [b] Concentrations are initial values in molar units.

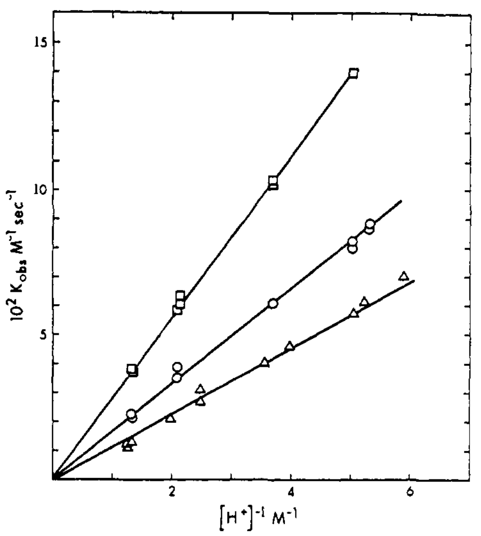

Figure 6. Dependence of reduction rate of $(NH_3)_5CoNH_2\ CHO^{3+}$ by Cr^{2+} on $[H^+]$, μ = 0.92 *M* ($LiClO_4$): △, 25.5°; ○, 34.6°; □, 44.4°.

The products are Co^{2+}(aq), NH_4^+, and a chromium(III) complex, which is not $Cr(OH_2)_6^{3+}$, as shown by ion exchange experiments discussed later. This mechanism gives the rate law

$$\frac{-\mathrm{d}\ln[(NH_3)_5CoNH_2CHO]}{\mathrm{d}t} = \frac{k_{NH}K_a}{K_a + [H^+]}[Cr^{2+}] \qquad (3)$$

Under the conditions of the kinetic study $[H^+] \gg K_a$; therefore by comparison of eq 2 and 3, $k' = k_{NH}K_a$. The specific rate constant k_{NH} has been determined from the experimental values of k' and K_a at different temperatures. The results are given in Table V.

An acid-independent term in the rate law for reduction of the N isomer could correspond to the rate of reduction of $(NH_3)_5CoNH_2CHO(k_{NH_2})$. This term would appear as the intercept on a plot such as Figure

Table IV. Kinetic Data for the Reduction of the Oxygen-Bound Formamide and N,N-Dimethylformamide Complexes of Pentaamminecobalt(III) by Chromium(II)[a]

Ligand	[Oxidant] × 10^3 [b]	[Reductant] × 10^2 [b]	$[H^+]$[b]	Temp, °C	$k_{obsd} \times 10^2$, M^{-1} sec^{-1}
$OCHNH_2$	2.00	3.17	0.208	26.0	0.83
$OCHNH_2$	2.20	3.90	0.200	26.0	0.87
$OCHNH_2$	1.43	3.90	0.207	26.0	0.85
$OCHNH_2$	2.28	5.72	0.791	36.0	1.68
$OCHNH_2$	2.00	3.71	0.149	36.0	1.51
$OCHNH_2$	1.95	3.17	0.093	36.0	1.69
$OCHNH_2$	2.35	3.90	0.303	36.0	1.48
$OCHNH_2$	1.95	3.17	0.592	36.0	1.50
$OCHNH_2$	2.04	4.45	0.805	36.0	1.59
$OCHNH_2$	2.17	5.57	0.207	36.0	1.66
$OCHNH_2$	2.00	3.71	0.149	46.0	2.96
$OCHNH_2$	1.59	3.71	0.303	46.0	2.96
$OCHNH_2$	2.37	3.71	0.860	46.0	2.96
$OCHN(CH_3)_2$	0.90	3.98	0.074	32.6	0.72
$OCHN(CH_3)_2$	1.80	2.14	0.961	32.6	0.75
$OCHN(CH_3)_2$	1.80	2.14	0.077	32.6	0.82
$OCHN(CH_3)_2$	1.90	2.30	0.961	44.6	1.60
$OCHN(CH_3)_2$	1.90	2.30	0.077	44.6	1.60
$OCHN(CH_3)_2$	1.80	2.14	0.077	54.1	2.63
$OCHN(CH_3)_2$	1.80	2.14	0.077	54.1	2.51

[a] For all runs ionic strength μ = 1.0. [b] Concentrations are initial values in molar units.

Table V. Summary of Equilibrium and Kinetic Parameters

Ligand	Temp, °C	10^3K_a, M	$k' = k_2K_a$, sec^{-1}	k_2, M^{-1} sec^{-1}	$\Delta H_2^{\ddagger}$, kcal mole^{-1}	$\Delta S_2^{\ddagger}$, eu
Formamide	25.5	6.92	1.20×10^{-2}	1.74	12.0	−17
N-bonded	34.6	5.36	1.61×10^{-2}	3.00	±2.0[a]	±6[a]
	44.4	4.37	2.75×10^{-2}	6.30		
Formamide	26.0			0.0085	10.7	−32
O-bonded	36.0			0.0159	±1.0	±3
	46.0			0.0296		
DMF	32.6			0.0079	10.6	−33
O-bonded	44.6			0.0160	±1.0	±3
	54.1			0.0257		

[a] The errors in this case include the error from K_a and k', each of which contributes $\sim\pm 1$ kcal mole^{-1} to $\Delta H_2^{\ddagger}$ and $\sim\pm 3$ eu to $\Delta S_2^{\ddagger}$. Errors are estimated assuming $a \pm 5\%$ error on the rate constants and $\pm 10\%$ on K_a, as indicated by the reproducibility of the results.

6. A least-squares analysis of the data indicates that k_{NH_2} is less than 1×10^{-3} M^{-1} sec^{-1}, and cannot be reliably established.

The rates of reduction of the O isomer and the DMF complex were found to be independent of hydrogen ion concentration and obey the rate law

$$\frac{-\mathrm{d}\ln[\mathrm{Co}^{3+}\text{ complex}]}{\mathrm{d}t} = k''[\mathrm{Cr}^{2+}] \qquad (4)$$

In this case k'' will correspond to the specific rate constant for the reaction of $(NH_3)_5CoOCHNH_2{}^{3+}$(k_O) and $(NH_3)_5CoOCHN(CH_3)_2{}^{3+}$ (k_{DMF}) with chromium(II). The rate data for the O isomer and DMF complex are summarized in Table IV. The specific rate constants and activation parameters are given in Table V.

The identification of the chromium(III) product of the reduction of the O and N isomers is most crucial in determining the point of attack of the reducing agent on the formamide ligand. For the N isomer, progress of the reaction was followed by repeatedly scanning the visible region of the spectrum. It was found that a maximum absorbance at 410 mμ was reached, which then lost intensity and shifted to 408 mμ. This indicates that a chromium(III) formamide complex is being formed, which them hydrolyzes to $Cr(OH_2)_6{}^{3+}$. These observations permitted the choice of optimum reactant concentrations to give the most chromium(III)–formamide product. The product solutions under such conditions were ion exchanged, and the visible spectrum of the chromium(III) product was recorded. Representative results of such experiments are given in Table VI.

Table VI. Electronic Spectra of Chromium(III) Reaction Product

Reaction	ϵ_{max}	λ_{max}, mμ	ϵ_{max}'	λ_{max}', mμ
$(NH_3)_5CoO{=}CHNH_2{}^{3+} + Cr^{2+}$ [a]	15.0	407	12.8	575
$(NH_3)_5CoNHCHO^{2+} + Cr^{2+}$ [b]	22.3	409	20.5	578
$Pb^{2+} + Cr^{2+} + O{=}CHNH_2$	21.0	409	19.9	578
$(NH_3)_5CoO{=}CHN(CH_3)_2{}^{3+} + Cr^{2+}$ [c]	15.3	408	13.5	575
$Cr(OH_2)_6{}^{3+}$ [d]	15.6	408	13.4	574

[a] $[Cr^{2+}]$, 0.115 *M*; [cobalt(III) complex], 0.009 *M*; $[H^+]$ = 0.582 *M*; reacted at 36.0° for 1 hr. [b] $[Cr^{2+}]$, 0.012 *M*; [cobalt(III) complex], 0.0108 *M*; $[H^+]$, 0.09 *M*; reacted at room temperature for 2 hr. [c] $[Cr^{2+}]$, 0.023 *M*; [cobalt(III) complex], 0.0018 *M*; $[H^+]$, 0.077 *M*; reacted at 44° for 2 hr. [d] J. A. Laswick and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3564 (1959).

The extinction coefficient of the product shows that it is not $Cr(OH_2)_6{}^{3+}$, and the peak positions seem most consistent with those expected for an O-bonded formamide complex. The acid form of the Cr–N-bonded isomer would be expected to have a spectrum similar to $(H_2O)_5CrNH_3{}^{3+}$,[12] which has absorption maxima at 547 and 397 mμ. This expectation is based on analogy to the spectra of the $(NH_3)_5$Co–formamide isomers and is also consistent with results on the chromium(II)–isonicotinamide system.[13]

The chromium–formamide complex was also prepared by the reaction of lead(II) (0.032 *M*) and chromium(II) (0.067) in aqueous formamide (0.075 *M*). The characteristics of the visible spectrum of the chromium(III) product (obtained after elution from Dowex-50X8) are given in Table VI and appear identical, within experimental error, with those from the reduction of the N isomer with chromium(II). The same product was also obtained by treating aqueous chromium(III) perchlorate and formamide at room temperature for 3 days and then separating the mixture by ion exchange. A qualitative test[14] for formamide was positive on the ion exchanged product from all three methods of preparation.

For the O isomer, repeated scans of the visible spectrum for reactants at approximately 1:1 concentrations (Figure 7) showed the growth of two maxima at 408 and 575 mμ, which did not lose intensity with time. Four isosbestic points at 388, 432, 573, and 642 mμ further confirm the existence of only one product. This product was found to be $Cr\ (OH_2)_6{}^{3+}$ by ion exchange. Such results are not consistent with hydrolysis of an initial Cr(III)–O isomer product.

Similar behavior was found for the DMF complex, the product after ion-exchange being $Cr(OH_2)_6{}^{+3}$. This result is consistent with the previous work of Gould. Three good isosbestic points are observed at 387, 437, and 573 mμ.

Conclusion

The results of the product analysis of the chromium(II) reduction of the N-bonded isomer do not prove conclusively the position of attack of the reducing agent on the formamide ligand. The possibility remains that the O-bonded chromium(III) product might have resulted from rapid linkage isomerization of an initial N-bonded chromium(III) product. The linkage isomerism might occur by internal rearrangement, or by chromium(II)–(III) electron transfer. The former mechanism seems rather unlikely in view of the sta-

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(12) J. H. Espenson and D .W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

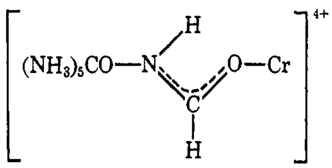
(13) F. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1163 (1968).

(14) S. Soloway and A. Lipschitz, *Anal. Chem.*, **24**, 898 (1952).

bility of the pentaamminecobalt(III) linkage isomers, and the electron transfer mechanism would not be expected to be rapid, judging from the study of Deutsch and Taube[15] on acetatopentaaquochromium(III) with chromium(II).

When the results from the O-bonded isomer are considered, however, it becomes clear that attack at the atom directly bonded to cobalt(III) (oxygen in this case) does not occur. If attack at oxygen had occurred, then the chromium(III)-oxygen-bonded product should have resulted. However, this reaction produced only $Cr(OH_2)_6^{3+}$, probably by an outer sphere mechanism.

It is concluded that the results from the O-bonded isomer rule out attack of chromium(II) on the atom adjacent to cobalt(III). The product from reduction of the N-bonded isomer, $(NH_3)_5CoNHCHO^{2+}$, indicates that chromium(II) attack occurs at the formamide oxygen atom. The activated complex might be pictured as



The fact that the O-bonded formamide and DMF complexes are reduced without ligand transfer may be attributed to the nonavailability of a lone pair of electrons on the remote nitrogen atom in both complexes. This lone pair may be necessary to form the bond to chromium(II) in the bridged activated complex. In the O-bonded complexes the nitrogen lone pair is drawn into the O=C—N π system by the electron withdrawing $(NH_3)_5Co^{3+}$, and is therefore not available for bonding to chromium(II).

The observation that the conjugate base of the N isomer is reduced much more rapidly than its parent acid may provide a hint as to the electron transfer path. It might be argued that this rate enhancement is due to attack by the reducing agent at the nitrogen lone pair in the conjugate base. However, this is contrary to the previous arguments and also does not explain why the O-bonded isomers are reduced without ligand transfer, since in the latter a lone pair is always available on the oxygen atom. Therefore, it seems that the greater rate of reduction of the conjugate base of the N isomer may be associated with the ability of the nitrogen to π-bond with the carbon. This may provide more rapid electron transfer to the cobalt(III) or may provide a more stable radical-ion intermediate, in which the electron is delocalized in the formamide π-antibonding system.

On the basis of the previous arguments it is predicted that electron transfer should not occur readily through an $-NH_2$ group. If the lone pair of electrons on the nitrogen is available for bonding to the reducing agent, then there will not be a π system in conjugation with the nitrogen lone pair of electrons. On the other hand, if the lone pair is part of a conjugated system then it will not be available for bonding to the reducing agent. These predictions are consistent with the observations of Nordmeyer and Taube[13] on the chromium(II)–nicotinamidopentaamminecobalt(III) system, and those of Hurst and Taube[16] on the chromium(II) reduction of (methylamidofumarato)pentaamminecobalt(III).

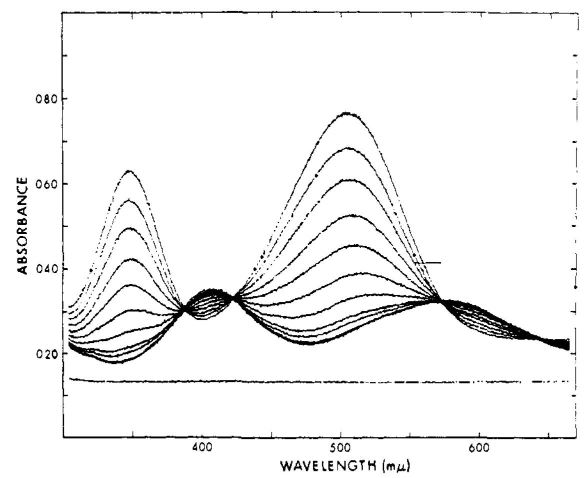


Figure 7. Change in visible spectrum during reduction of $(NH_3)_5CoOCHNH_2^{3+}$ (0.011 M) by Cr^{2+} (0.919 M; $[H^+]$ = 0.505 M; 28.5°; μ = 0.99 M. The absorbance is decreasing at ~500 mμ and ~350 mμ due to consumption of Co^{3+} complex, and increasing at ~600 mμ and ~410 mμ due to production of $Cr(OH_2)_6^{3+}$. Isosbestic points occur at 388, 432, 573, and 642 mμ. The spectral scans were started at 4, 22, 45, 80, 121, 180, 262, 460, 645, 763, and 1436 min after mixing. The last three show no change.

It was noted, however, that Fraser[17] had reported that the reduction of carbamatopentaamminecobalt(III) by chromium(II) proceeds by electron transfer through nitrogen, with production of a nitrogen bonded chromium(III) product. During attempts to reproduce this work the authors have found that the product has a visible spectrum typical of an O-bonded chromium(III) complex.[18] The observed second-order rate constant shows an inverse dependence on $[H^+]$ and may be described by the equation $k_{obsd} = (0.20 + 0.097[H^+]^{-1})$ M^{-1} sec^{-1} at 26°; μ, 1.0 M ($LiClO_4$).[18a] The latter result conflicts with the first-order acid dependence reported by Fraser. There is no apparent explanation for these discrepancies, but after extensive characterization[19] of the complex, one feels confident that it conforms to the predictions made above and produces only an O-bonded chromium(III) product.

Acknowledgment. The authors wish to acknowledge financial support, and fellowship support to R. J. B., from the National Research Council of Canada.

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(15) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

(16) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1178 (1968).

(17) R. T. M. Fraser, *Inorg. Chem.*, **3**, 1561 (1964).

(18) The ion-exchanged product shows maxima at 568 mμ (ϵ 23.9) and 414 (21.0).

(18a) NOTE ADDED IN PROOF. Recent work over a wider acid range indicates that, at 25.6°, $k_{obsd} = (0.208 + 0.045[H^+])(0.083 + [H^+])^{-1}$ M^{-1} sec^{-1}.

(19) The complex has been characterized by C, H, and N analysis and visible and nmr spectroscopy, all of which provide quantitative evidence for the expected composition.